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An Investigation of Unique Metal Complexes Produced

Using Polystyrene-2,2'-bipyridine as a Support,

and Several Hydrogenation Catalysts Derived from This Copolymer

by **LEVEL** II

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Russell S. Drago, Eric D. Nyberg and A. G. El A'mma

Abstract

The cleavage reaction between polystyrene bound pyridine and
2,2'-bipyridine ligands, (P)-py and (P)-bipy, and the dimers
$(Rh(X)(CO)Cl)_2$ (X = CO, $(C_6H_5)_3P$, or tolyl$_3$P) were studied. While the
(P)-py cleavages produced products analogous to those found homo-
geneously, the reactions using (P)-bipy resulted in the formation
of several metal complexes not found in solution. This is at
least in part the result of the accessability of the initially
formed (P)-bipy-rhodium complexes to subsequent reactions which
cannot occur in the homogeneous case due to precipitation of the
rhodium complex initially formed. These supported rhodium systems,
as well as (P)-bipyPdCl$_2$ and (P)-bipyPtCl$_2$, were investigated as
hydrogenation catalysts. In the case of the former two systems it
was found that metal aggregates were formed. This was surprising
in light of the general stability of bipyridine complexes. The
(P)-bipyPtCl$_2$ system is an active catalyst for the hydrogenation
of a number of substrates. Metal formation did not occur in this
case.

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INTRODUCTION

Much emphasis has been placed on demonstrating the usefulness
of supporting metal complexes on functionalized polymers with
regard to producing systems with unique chemical behavior. While
this "heterogenization" is in itself advantagous in the case of
catalytic systems, it has long been recognized that the support
may be made to more directly influence chemical reactivity. This
influence may be divided into active and passive categories. The
substrate size selectivity exhibited by many polymer supported
catalysts[1] is an example of an active polymer role. Site isola-
tion of a complex, to inhibit metal dimer or cluster formation, is
an example of a passive role by a support. Passive polymer influence
is not limited to cases of effective site isolation. The precip-
itation of a solid product from a homogeneous solution provides a
barrier to a more complete reaction (whether it be a thermodynamic
or kinetic barrier). The dispersal of the product over a func-
tionalized polymer will prevent crystalization, leaving it vulnerable
to further reactivity. If subsequent reactions do occur, any
direct analogy drawn between solution and polymer bound products
is of limited usefulness. However, in this case novel complexes
may be formed which are unique to the heterogenized phase.

We report here our studies of the bridge splitting reactions
between polystyrene bound pyridine, $\text{\textcircled{P}}$-py, and polystyrene bound
2,2'-bipyridine,[2] $\text{\textcircled{P}}$-bipy, with the dimers $[Rh(X)(CO)Cl]_2$
(where X denotes CO, $(C_6H_5)_3P$, or $tolyl_3P$). The reactions with
$\text{\textcircled{P}}$-bipy provide a good example of the passive metal dispersal
function the polymer may provide. In addition, the $\text{\textcircled{P}}$-bipy

polymer seems to play an active role in influencing the reaction products. The attachment of the 2,2'-bipyridine group to the polystyrene support is expected to lead to it's binding via the C(6) [3] (adjacent to one nitrogen donor atom). This may result in a steric weakening of one of the (P)-bipy nitrogen bonds to rhodium, and lead to the potential for monodentate coordination. Further support for the existance of such an effect exists from a study of the first stepwise formation constants for binding pyridine, 4-phenylpyridine, and 2-phenylpyridine to aquated copper(II).[4] As a result of both the passive and active influence of the polystyrene support in our systems, several unique metal complexes were prepared and characterized.

Also investigated were the activities of these (P)-bipy supported rhodium complexes, as well as (P)-bipyMCl$_2$ complexes (M = Pt, Pd), in the catalytic hydrogenations of a number of substrates. Since coordination of metals to polymers functionalized with unidentate ligands many times results in significant metal leaching into solution, the bidentate (P)-bipy ligand seemed attractive. Card and Neckers have prepared a number of metal complexes with this support, and reported then to be quite stable.[2] In addition, similar enthalpies of adduct formation[5] for the sigma donor properties of pyridine and tri-p-tolylphosphine (tolyl$_3$P) led us to suspect that bipyridine might function in a manner similar to phosphines in catalytic systems. Bipyridine is a slightly better sigma donor and a poorer π-acceptor than tolyl$_3$P. Both of these effects should enhance the tendency of the metal to undergo oxidative addition reactions. Finally, any tendency of the (P)-bipy ligand toward monodentate coordination due to steric interference

from the polymer attachment would contribute to a greater degree of metal coordinative unsaturation, and therefore to more facile substrate or H_2 coordination in the hydrogenation reaction.

EXPERIMENTAL

2% crosslinked polystyrene gel resin (200-400 mesh) was purchased from Bio-Rad. The 5% (60-80 mesh) and 8% (80-150 mesh) crosslinked polystyrene gel resins, as well as the polystyrene-pyridine copolymer, (P)-py, were prepared by the suspension technique reported previously[6] (the (P)-py was prepared from 4-vinylpyridine directly). Polystyrene-2,2'-bipyridine samples were prepared as described by Neckers et al.[2] The resultant beads were soxhlet extracted two days, and oven dried. The rhodium precursors where prepared as reported in the literature.[7,8]

Infrared spectra were recorded on a Perkin Elmer Model 599B, and glc spectra were obtained using a Varian Model 940 FID instrument using a one meter, 1/16 inch I.D. copper column packed with Chromasorb P supported diethylene glycol adipate set at 50°C. Components were identified by injecting authentic samples and comparing retention times.

(P)-(bipy)MCl$_2$ (M = Pt and Pd)

1.0g polymer bound bipyridine, (P)-bipy, was added to a filtered solution of 0.1 g $(C_6H_5CN)_2MCl_2$[9] in acetone (30 ml) and the mixture refluxed for 12 hours. After cooling, the beads were collected by suction, soxhlet extracted with acetone, and air dried. Elemental analysis for (P)-bipy PtCl$_2$: 0.93% Pt; 0.45% Cl. For (P)-bipy PdCl$_2$: 0.83% Pd; 0.92% Cl.

Polystyrene Dispersed Palladium Metal

The polymer (P)-bipy PdCl$_2$ (500 mg) was added to a stirred solution of 1,4-dioxane (50 ml), 95% hydrazine (5 ml) and absolute ethanol (5 ml). After 12 hours of stirring at room temperature,

the black beads were collected by suction, washed with ethyl acetate-benzene (1:1), ethanol, and air dried.

(P)-py-rhodium and (P)-bipy-rhodium Species

The following general procedure was used to graft Rh(I) species onto (P)-bipy and (P)-py using $[Rh(CO)_2Cl]_2$, $[Rh(tolyl_3P)-(CO)Cl]_2$ and $[Rh(C_6H_5)_3P)(CO)Cl]_2$ as starting materials. The polymer (0.50 g) was added to 30 ml toluene at room temperature. After purging the system with bubbling argon for 30 minutes, the chloro bridged rhodium dimer (30 mg) was added and the mixture stirred for 24 hours under Ar. The brown beads were collected by suction, washed with toluene, absolute ethanol, soxhlet extracted with toluene, and air dried.

Hydrogenation Procedure

All catalytic runs were carried out in a 250 ml Parr pressure bottle equipped with a 200 psi Marsh pressure gauge and gas inlet-outlet tube for filling and purging. The bottle-copper tubing interface was sealed by a tightly clamped silicone rubber stopper. No pressure drop occurred from the sealed system in 24 hours on pressurization to 120 psi at either RT or 120°C. The apparatus was checked regularly for leaks to insure there were no spurrious pressure drops.
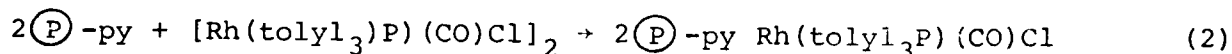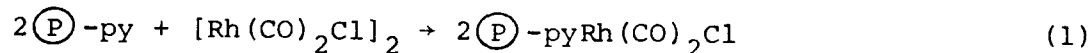
The following procedure is typical of that followed in the catalytic hydrogenations. The polymer sample (50 mg), substrate (5 ml), benzene solvent (30 ml), and a stir bar were loaded into the 250 ml Parr bottle, hooked to the pressurization apparatus, and purged by six repetitions of bottle pressurization to 100 psiH$_2$,

and gas discharging. The bottle was then pressurized to 100 psi H_2 (at RT), and immersed in a preheated oil bath to begin the reaction. After 24 hours the bottle was removed from the bath, cooled to RT, the final pressure recorded, and the filtrate analyzed for products.

RESULTS AND DISCUSSION

I. Preparation and Characterization of Supported Rhodium Systems

While in solution the cleavage reactions with both homogeneous 2,2'-bipyridine and pyridine[8] are straightforward, the reaction of (P)-bipy with these dimers proved to be somewhat more involved. The (P)-py cleavage resulted in products analogous to those formed in the homogeneous phase, as evidenced by their infrared spectra (reactions (1) and (2)).

$$2(P)\text{-py} + [Rh(CO)_2Cl]_2 \rightarrow 2(P)\text{-pyRh(CO)}_2Cl \tag{1}$$

$$2(P)\text{-py} + [Rh(tolyl_3)P)(CO)Cl]_2 \rightarrow 2(P)\text{-py Rh(tolyl}_3P)(CO)Cl \tag{2}$$

The infrared carbonyl absorbtion frequencies for all carbonyl containing species characterized in this study are listed in Table I. The pyridine and (P)-py cleavage products from reaction (1) exhibited two equal intensity CO stretching bands.

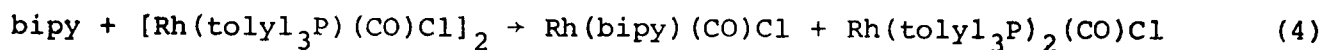The reaction between (P)-bipy and $[Rh(CO)_2Cl]_2$ was more complicated. The infrared spectrum in the carbonyl stretching region is displayed in Figure 1. The observation of two bands may be explained by either a dicarbonyl product, such as a monodentate (P)-bipy supported specie $((P)\text{-bipy})_m Rh(CO)_2Cl)$, or two distinct CO containing products. The homogeneous reaction produces only the deep purple solid, Rh(bipy)(CO)Cl (isolated in 95% yield) (reaction (3)).

$$bipy + [Rh(CO)_2Cl]_2 \rightleftharpoons 2Rh(bipy)(CO)Cl + 2CO \tag{3}$$
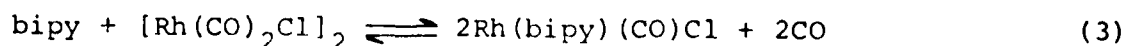
Polymer attachment via the 6-position of the bipyridine ligand may be expected to contribute to a weakening in the adjacent nitrogen

coordination to rhodium via steric interference, and monodentate coordination of (P)-bipy could result as shown in the proposed structure of ((P)-bipy)$_m$Rh(CO)$_2$Cl (Figure 2). The infrared CO band positions in Figure 1 are similar to those for (P)-pyRh(CO)$_2$Cl. The much greater intensity of the 1990 cm^{-1} band in the (P)-bipy product is due to the contribution form bidentate (P)-bipyRh(CO)Cl (vide infra).

The homogeneous reaction between 2,2'-bipyridine and [Rh-(tolyl$_3$P)(CO)Cl]$_2$ proceeds stoichiometrically as shown in reaction (4).

$$\text{bipy} + [\text{Rh}(\text{tolyl}_3\text{P})(\text{CO})\text{Cl}]_2 \rightarrow \text{Rh}(\text{bipy})(\text{CO})\text{Cl} + \text{Rh}(\text{tolyl}_3\text{P})_2(\text{CO})\text{Cl} \qquad (4)$$

The Rh(bipy)(CO)Cl was isolated in 90% yield, and the Rh(tolyl$_3$P)$_2$-(CO)Cl in solution was quantitatively detected using visible spectroscopy. The reaction between (P)-bipy and [Rh(tolyl$_3$P)(CO)Cl]$_2$ was much slower, and its progress was monitored by infrared scans of bead samples in the CO region as a function of reaction time (Figure 3). During the course of this reaction the beads progressively changed from gold to dark brown in color. It is apparent from the strong band at 1990 cm^{-1} in Figure 3 that the predominant carbonyl containing supported complex is a monocarbonyl, characterized as (P)-bipyRh(CO)Cl by analogy with the homogeneous reaction (reaction (4)). Rh(tolyl$_3$P)$_2$(CO)Cl was detected in the final solutions by visible spectroscopy.

A quantitative analysis of the Rh(tolyl$_3$P)$_2$(CO)Cl and [Rh-(tolyl$_3$P)(CO)Cl]$_2$ in the final solution and the rhodium and phosphorus on the final beads revealed that the (P)-bipy analogue of reaction (4) was by no means the exclusive process. These re-

sults are presented in Table II. The rhodium content on the beads was determined from the visible spectra of the final solutions by assuming that all rhodium not accounted for by the $Rh(tolyl_3P)_2$-$(CO)Cl$ and $[Rh(tolyl_3P)(CO)Cl]_2$ in solution was bound to the ⓟ-bipy beads. This assumption was supported by both the excellent fits in the simulation of the visible spectra and the good agreement between the supported rhodium contents calculated in this manner and those determined by neutron activation analyses on selected samples.

For all samples prepared the amount of rhodium bound to the beads was greater than could be explained by the polymer analogue of reaction (4). In fact for different samples reaction (4) could account for only 20% to 80% of the rhodium actually coordinated to the ⓟ-bipy support (determined from the $Rh(tolyl_3P)_2(CO)Cl$ found in the final solution). Therefore, a second reaction must be involved in which the net result is the coordination of both rhodium centers of the $[Rh(tolyl_3P)(CO)Cl]_2$ dimer to ⓟ-bipy groups. In addition, since free phosphine in solution will cleave the dimer to form $Rh(tolyl_3P)_2(CO)Cl$,[8] all phosphine not found in solution as $Rh(tolyl_3P)_2(CO)Cl$ and $[Rh(tolyl_3P)(CO)Cl]_2$ must be bound to the polymer via coordination to rhodium. The values for the bead's predicted phosphorus contents are listed in the table, as are those found by elemental analyses. This second process is represented in reaction (5).

$$2 \text{ⓟ-bipy} + [Rh(tolyl_3P)(CO)Cl]_2 \rightarrow 2 \text{ⓟ-bipyRh}(tolyl_3P)Cl + 2CO \qquad (5)$$
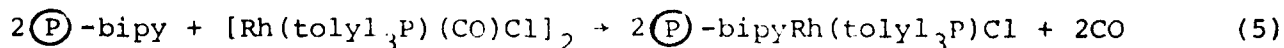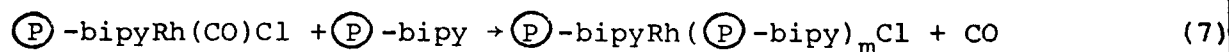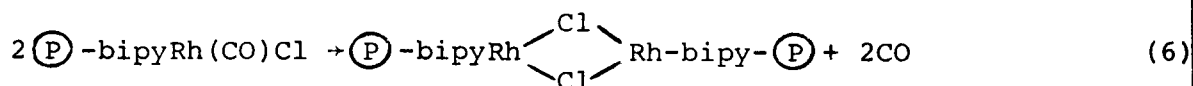
For sample Ia reaction (5) accounts for only 20% of the rhodium, while for sample IIIa it accounts for 80%.

Since reaction (5) represents a process unique to the polymer supported bipyridine ligand, a closer examination was made. Two fundamental mechanisms are possible: 1) a direct or "concerted" formation with loss of CO, or 2) an indirect process involving the intermediate formation of (P)-bipyRh(CO)Cl. The infrared evidence in Figure 3 serves as strong evidence for the second mechanism. At 15 minuts of reaction a very strong CO band at 1990 cm^{-1} is observed, characteristic of (P)-bipyRh(CO)Cl. Samples scanned at 35 and 75 minutes exhibit progressively less intense bands. After this the 1990 cm^{-1} band grows in intensity, along with a weak band at 2065 cm^{-1}. As diagrammed in Scheme 1, this may be explained by the initial exclusive formation of (P)-bipyRh(CO)Cl, and subsequent competition for free tolyl$_3$P by (P)-bipyRh(CO)Cl and [Rh(tolyl$_3$P)-(CO)Cl]$_2$. Since step 1 in the scheme produces only (P)-bipyRh(CO)Cl and free tolyl$_3$P, the immediate growth of the 1990 cm^{-1} band is expected. As the concentration of free phosphine builds up in the polymer matrix, steps 2 and 3 in the scheme, which both liberate CO from the polymer, would become increasingly competitive, resulting in a decrease in the 1990 cm^{-1} band intensity. Step 4 consumes the free phosphine, thus reducing the potential for CO displacement in steps 2 and 3. Further substantiation of the scheme comes from an examination of Table II. Sample Ia, produced from 2% crosslinked resin (200-400 mesh), possesses only 20% supported phosphine complex. Samples IIIa, IIIb and IIIc are produced from 8% crosslinked resin (80-150 mesh), and possess from 55% to 80% phosphine complex. The lower crosslinking of sample Ia will result in larger pore sizes on swelling in toluene.

This, in addition to the much smaller bead diameters of sample Ia, will result in faster diffusion rates for all solution species within the resin relative to those for samples IIIa, IIIb and IIIc. The effect is greater access of free phosphine to $[Rh(tolyl_3P)(CO)Cl]_2$ for sample Ia, and hence a decrease in the total amount of phosphine which may eventually coordinate to the polymer bound rhodium.

Steps 2 and 3 in the scheme were substantiated by the reaction of sample Ia with excess phosphine. A small amount of $Rh(tolyl_3P)_2(CO)Cl$ and a polymer supported rhodium complex with a 1:1 ratio of rhodium to phosphorus (sample Ib) characterized as (P)-bipyRh(tolyl$_3$P)Cl, was produced. The homogeneous reaction between Rh(bipy)(CO)Cl and two equivalents of phosphine produces $Rh(tolyl_3P)_2(CO)Cl$ and free 2,2'-bipyridine stoichiometrically. The irreversibility of step 2 was demonstrated by carbonylating sample Ib in toluene at RT under 100psi CO, resulting in only a very weak infrared band. In contrast, the carbonylation of sample IIg under identical conditions resulted in two medium strength bands at 2065 and 1990 cm^{-1}, which are assigned to ((P)-bipy)$_m$Rh(CO)$_2$Cl. This specie is also unique to the (P)-bipy ligand. Indeed a small amount of this dicarbonyl complex is evident after 24 hrs of reaction between (P)-bipy and [Rh(tolyl$_3$P)-(CO)Cl]$_2$ (Figure 3). This could be produced from the CO liberated in step 2 of the scheme.

The lability of the CO ligand in (P)-bipyRh(CO)Cl is demonstrated by its complete loss during soxhlet extraction in THF (Figure 3). In the absence of free phosphine this may be explained by reactions (6) and (7), or reaction with oxygen.

$$2\,\text{\textcircled{P}}\text{-bipyRh(CO)Cl} \rightarrow \text{\textcircled{P}}\text{-bipyRh}\underset{\text{Cl}}{\overset{\text{Cl}}{<}}\!\!\!\!>\text{Rh-bipy-\textcircled{P}} + 2\text{CO} \qquad (6)$$

$$\text{\textcircled{P}}\text{-bipyRh(CO)Cl} + \text{\textcircled{P}}\text{-bipy} \rightarrow \text{\textcircled{P}}\text{-bipyRh(\textcircled{P}-bipy)}_m\text{Cl} + \text{CO} \qquad (7)$$

The low values for phosphorus found by elemental analyses (Table II) are attributed to the unreliability of the analyses at these low concentrations. Throughout the remainder of this paper the final supported rhodium complex will be referred to as ⓟ-bipyRhXCl.

In the homogeneous reaction the insolubility of Rh(bipy)(CO)Cl provides a driving force for the exclusive formation and isolation of this bipyridine product. In the polymer supported system this stabilizing influence is not present and subsequent reactions of ⓟ-bipyRh(CO)Cl occur. These findings emphasize two important statements about this area of chemistry. First, species can be prepared on the polymer whose solution counterpart does not exist. Second, it is not always safe to infer reactivity on a polymer support from analogous solution chemistry.

II. Catalytic Hydrogenations

A) Hydrogenations with ⓟ-bipyPtCl$_2$

The results of the catalytic hydrogenations using ⓟ-bipyPtCl$_2$ are presented in Table III. It is evident that this supported complex possesses a high degree of selectivity towards the hydrogenation of terminal olefins. The size and chemical similarities of the substrates studied indicates this selectivity is not due to differences in their diffusion rates through the polymer. It is most likely a result of the differences in rates of formation of sigma alkyl-rhodium complex intermediates. For example the binding constants for the formation of primary sigma alkyls are ca. fifty

times as great as those for the formation of corresponding secondary alkyls.[10]

An induction period of at least five hours was observed prior to all catalytic runs (using 50psi H_2, at 70°C). This was the case for recycled catalyst samples as well as fresh samples. The ability to recycle these supported catalysts as well as the colorless filtrates indicates leaching is unimportant. The absence of catalysis of the nitrobenzene hydrogenation to aniline by the ⓟ-bipyPtCl$_2$ product, which is characteristic of supported platinum metal (on charcoal)[11], eliminates consideration of the metal as the active catalyst here.

Bailar and Brunner[12] have supported platinum (II) chloride on macroreticular polystyrene which was previously functionalized with pendant tertiary phosphine ligands. Their findings indicate that in order for the platinum polymer system to be catalytic reaction conditions of 150°C, 550psi of H_2, and the addition of tin(II) chloride were needed. The polystyrene-bipyridine support provides a system which is active under much milder conditions.

B) Hydrogenations with ⓟ-bipyPdCl$_2$

The results of the hydrogenations catalyzed by ⓟ-bipyPdCl$_2$ are presented in Table IV. After one hydrogenation run the supported catalysts acquired a greenish coloration. The reduction of nitrobenzene to aniline indicates the formation of palladium metal under the conditions employed (70°C, 50psi H_2). A sample of polystyrene-bipyridine dispersed palladium metal was prepared by reduction of ⓟ-bipyPdCl$_2$ with ethanolic hydrazine. Electron microscopy revealed metal aggregates ranging up to 200Å in diameter, and the substrates 1-hexene, p-benzoquinone, and nitrobenzene, were readily

hydrogenated with this catalyst. The results in Table IV therefore must be considered to result from catalysis by a mixture of Ⓟ-bipyPdCl$_2$ and palladium metal.

Both the catalyst precursor (Ⓟ-bipyPdCl$_2$) and reaction conditions used here are different than those employed by Neckers et.al.[2] Their milder hydrogenation conditions (25°C, 1 atm H$_2$) would be expected to result in a reduced tendency to form metal crystallites. It is therefore not possible to draw any conclusions concerning metal formation in their system.

Neckers does propose that under his conditions Ⓟ-bipyPd(0) is formed, and is the active catalyst. This species may be monomeric or a metallic cluster. Bailar's study of (Ⓟ-P(C$_6$H$_5$)$_2$)$_2$-PdCl$_2$ catalyzed hydrogenations[12] is consistant with Pd(II) as the active catalyst. As noted by Neckers it would appear that the bipyridine ligand promotes the reduction of palladium(II) to the zero oxidation state. This possibility is further borne out in the Ⓟ-bipyRhXCl catalyzed hydrogenations (vide infra).

C) Hydrogenations with Ⓟ-bipyRhXCl Systems

The poorer π-accepting capabilities of bipy compared to phosphine, and the tendency of the Ⓟ-bipy ligand to coordinate in a monodentate fashion, should enhance the ability of Ⓟ-bipyRhXCl to undergo oxidative addition reactions compared to an analogous phosphine supported systems. Therefore the Ⓟ-bipy supported rhodium systems described earlier in this paper were investigated as 1-hexene hydrogenation catalysts. At 50°C and under 100psi H$_2$ using sample IIb an induction period of five to six hours was observed before H$_2$ uptake and 1-hexene hydrogenation to n-hexane occurred. Subsequent recycled catalyst exhibited no in-

duction period, in contrast to Ⓟ-bipyPtCl$_2$ recycling, and the
catalyst activity further increased. Cyclohexane and cyclohexene
were detected in the filtrate after the second catalytic run. These
products result from benzene hydrogenation, and are characteristic
of catalysis by rhodium metal. No benzene hydrogenation products
were detected by gas-liquid chromatography after the first use of
the supported catalyst, although complete conversion of 1-hexene
to n-hexane was realized at this stage.

A photoelectron spectroscopic analysis of a recycled polymer
sample capable of benzene hydrogenation detected binding energies
of 314.5 and 310.0 eV for the Rh $3d_{3/2}$ and $3d_{5/2}$ electrons, re-
spectively.[13] These do not correspond to either Rh metal (expected
to produce bands of 311.8 and 307.1) or Rh(I) species (producing
bands at 312.7-313.2 and 308.1-308.4), but do approach the values
expected for Rh(III) species (at 314.4 and 309.7 eV for RhCl$_3$·3H$_2$O).[14]
Freshly prepared samples of Rh metal on charcoal (from H$_2$ reduction
of RhCl$_3$) have been found to possess large amounts of Rh$_2$O$_3$ [15]
which would account for the ESCA results. Electron transmission
microscopy detected particles on the beads ranging from 20-40 Å in
diameter. Therefore it appears that rhodium metal forms on the
polymer as a result of H$_2$ reduction of the supported rhodium at 50
and 100°C, and that the 1-hexene hydrogenation may be explained by
it.

Hydrogenation of 1-hexene catalyzed by Ⓟ-bipyRh((C$_6$H$_5$)$_3$P)Cl
(sample Ib) at 100psi H$_2$ and 100°C also resulted in the formation
of a small amount of cyclohexane and cyclohexene, in addition to
n-hexane. Thus it appears this sample is reduced to rhodium metal
as well.

An investigation of the infrared spectra of the Ia sample after increasing treatment with 100psi H_2 at 50 and 100°C reveals that both the CO IR band (at 1990 cm^{-1}) and the 2,2'-bipyridine bands (at 1560 and 1580 cm^{-1}) are present through several stages of H_2 treatment (Figure 4). After a second treatment with H_2 at 100°C, the bipy bands decrease in intensity and the CO band disappears altogether. However, a significant amount of cyclohexane was formed during the first reduction at 100°C. The decrease in the 2,2'-bipyridine band intensities suggests the hydrogenation of this group to bipiperidine (loss of bipy form the hydrogenated polymer was ruled out by elemental analysis for N). This reduction is expected to cause increased metal center lability, and hence metal aggregation.

Catalysis with the supported Wilkinson's catalyst, Ⓟ-PPh$_2$-Rh(PPh$_3$)$_2$Cl (2% crosslinked gel resin; 200-400 mesh; 0.03 mmol Rh/g beads) under conditions similar to those used for the Ⓟ-bipy-rhodium samples was investigated (80psi H_2; 100°C; 24 hours reaction time). A small amount of cyclohexane was produced from the H_2 reduction of benzene solvent, again suggesting the formation of a small amount of rhodium metal. No detectable benzene hydrogenation products resulted from a hydrogenation of benzene using the homogeneous complex Rh((C$_6$H$_5$)$_3$P)$_3$Cl at 100psi H_2 and 100°C for 72 hours.

We obtained turnovers in the 1-hexene hydrogenation with Ⓟ-bipyRhXCl as great as 300 in first runs, without the attendant formation of detectable benzene hydrogenation products. This demonstrates an important point: the absence of aromatic hydrogenation products is not necessarily a valid criterion for ruling out cataly-

sis by small metal particles. This is of course a result of the
much greater reactivity of 1-hexene than benzene toward hydrogena-
tion.

These results also illustrate another point. With the excep-
tion of cases in which effective site isolation on a polymer has
been achieved, it should be considered that for many polymer sup-
ported transition metal systems there is considerable potential for
metal aggregation. The $\circled{P}$-P$(C_6H_5)_2$Rh$((C_6H_5)_3$P$)_2$Cl comparison to
the homogeneous Rh$((C_6H_5)_3$P$)_3$Cl system above is a good example.

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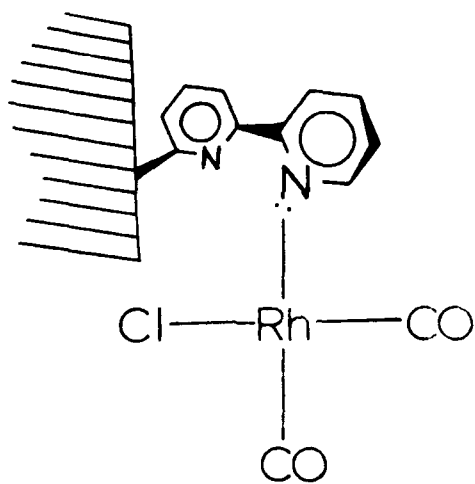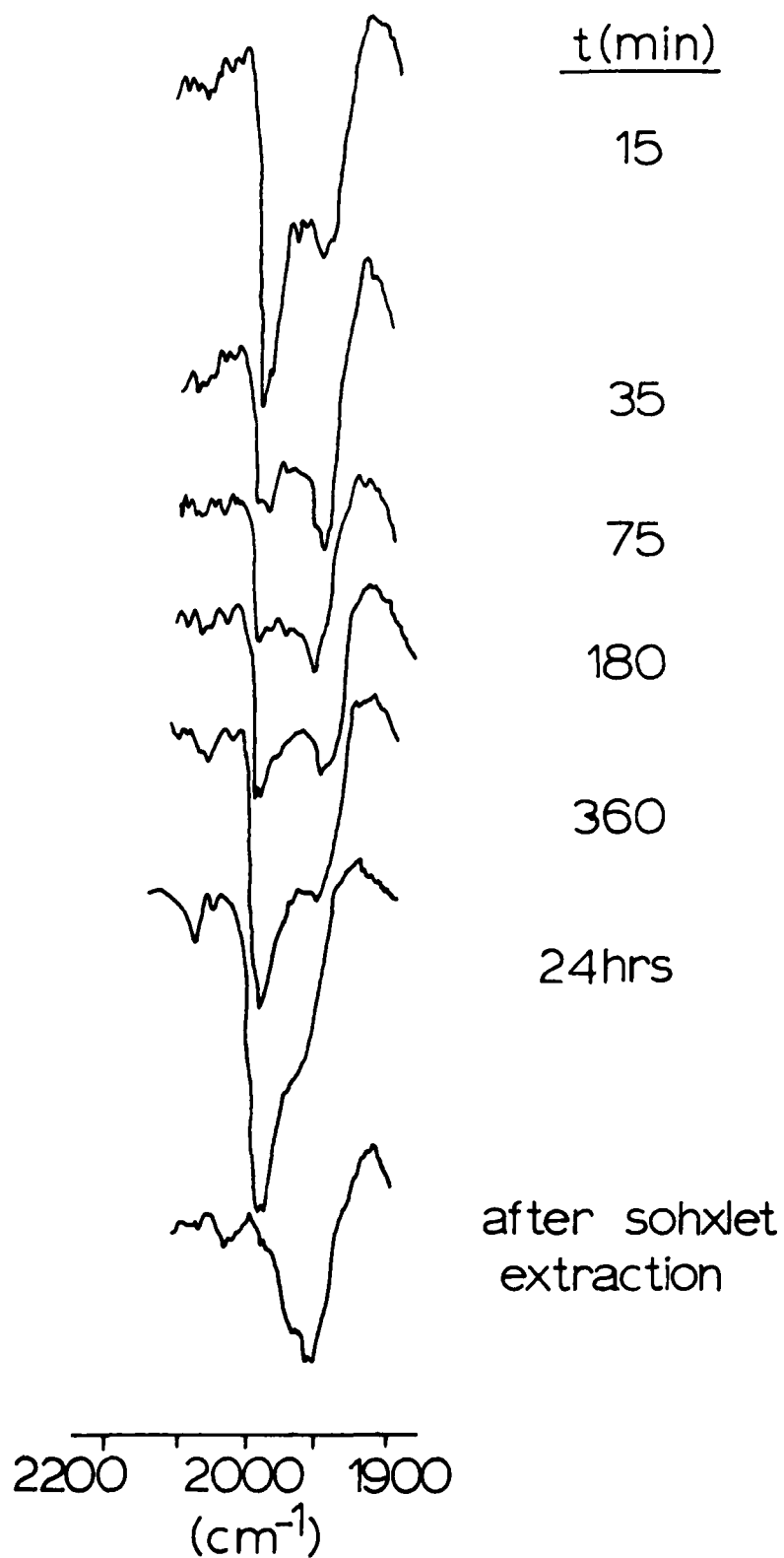1. Grubbs, R.H.; Kroll, L. C.; Sweet, E. M., J. Macromol. Sci.-Chem., 1973, A7(5), 1047.

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1. $2\,\text{\textcircled{P}}$-bipy + $[\text{Rh}(\text{tolyl}_3\text{P})(\text{CO})\text{Cl}]_2 \rightarrow 2\,\text{\textcircled{P}}$-bipyRh(CO)Cl + $2\text{tolyl}_3\text{P}$

2. $\text{\textcircled{P}}$-bipyRh(CO)Cl + $\text{tolyl}_3\text{P} \rightarrow \text{\textcircled{P}}$-bipyRh$(\text{tolyl}_3\text{P})$Cl + CO

3. $\text{\textcircled{P}}$-bipyRh(CO)Cl + $2\text{tolyl}_3\text{P} \rightarrow \text{\textcircled{P}}$-bipy + $\text{Rh}(\text{tolyl}_3\text{P})_2(\text{CO})\text{Cl}$

4. $[\text{Rh}(\text{tolyl}_3\text{P})(\text{CO})\text{Cl}]_2 + 2\text{tolyl}_3\text{P} \rightarrow 2\text{Rh}(\text{tolyl}_3\text{P})_2(\text{CO})\text{Cl}$

SCHEME 1.

Ⓟ - bipy

resin Ia

after first
treatment
(at 50 &
100°C)

after second
treatment

2000 1900 1700 1600

(cm⁻¹)
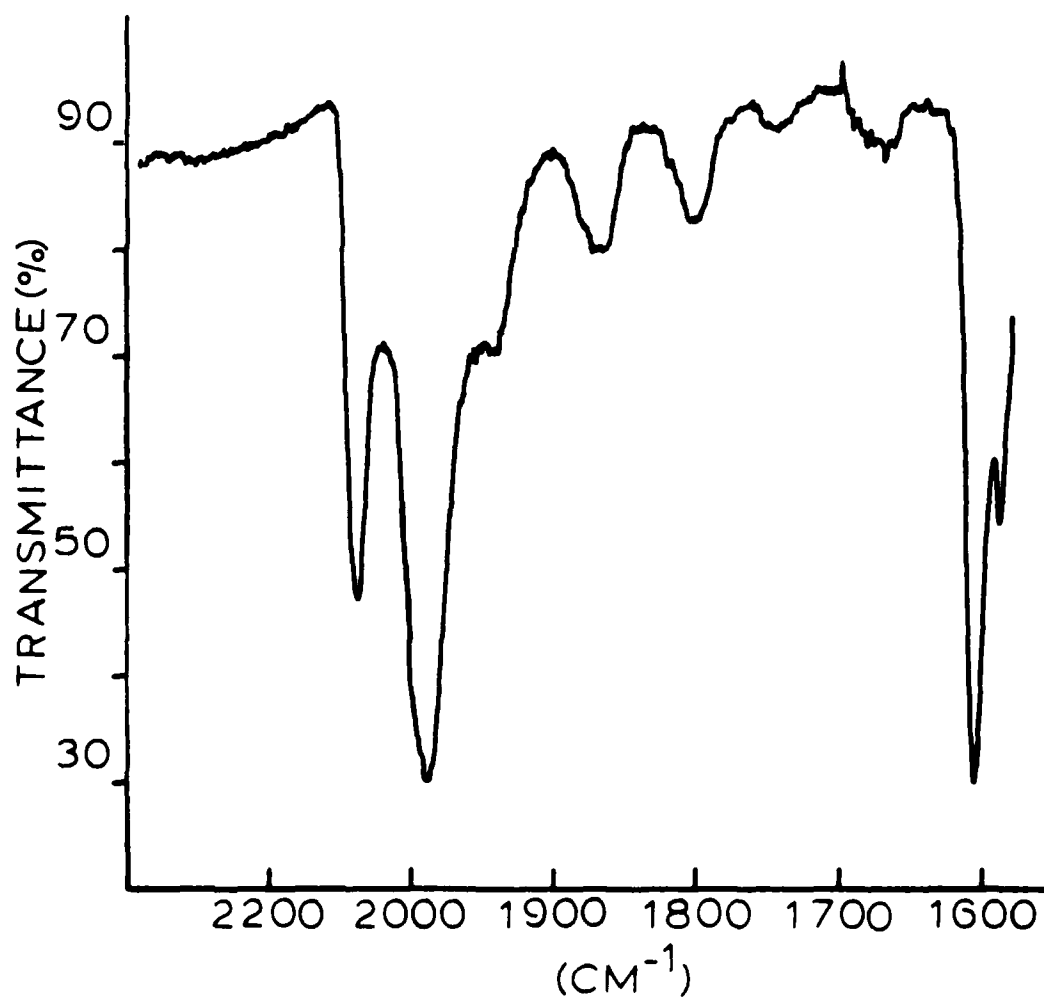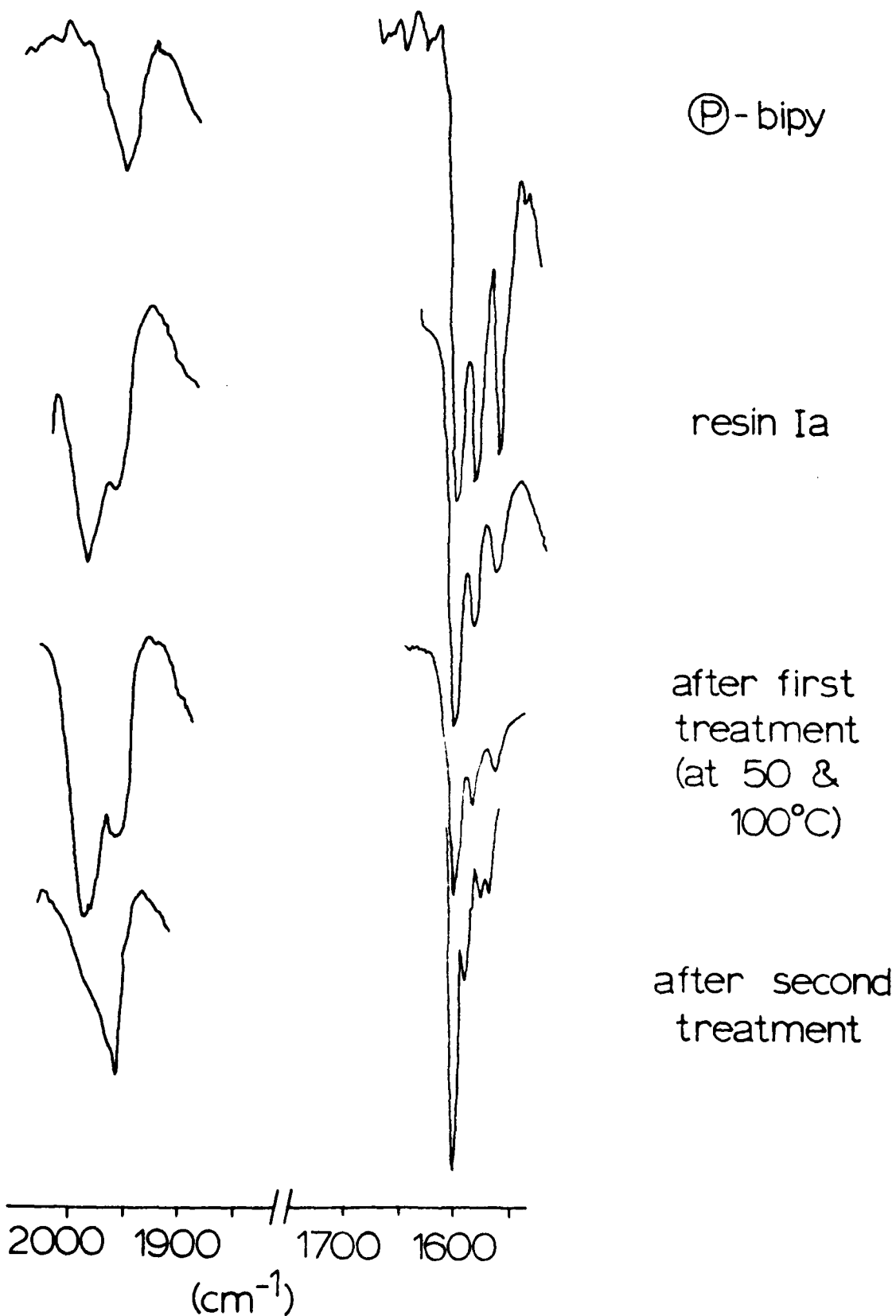
TABLE I.   Carbonyl Stretching Frequencies for Crystalline and
Polymer Supported Rhodium Complexes Studied.

Compound	Solvent	Bonds (cm^{-1})
$Rh(py)(CO)_2Cl$	$CHCl_3$	2090, 2015
ⓟ$-pyRh(CO)_2Cl$	Nujol	2080, 2000
$Rh(py)(tolyl_3P)(CO)Cl$		
ⓟ$-pyRh(tolyl_3P)(CO)Cl$	Nujol	1960
$[Rh(CO)_2Cl]_2$	Nujol	2105, 2089, 2036
$Rh(bipy)(CO)Cl$	Nujol	1958
ⓟ$-bipyRh(CO)Cl$	Nujol	1990
$(ⓟ-bipy)_mRh(CO)_2Cl$[a]	Nujol	2065, 1990

[a] The subscript m denotes monodentate coordination of the ⓟ-bipy ligand.

TABLE I.

Table II. Composition of Various Supported Polymers Used in This Investigation. (Substitution in Units of mmoles/g of Polymer.)

Sample	2,2'-bipyridine[a]	Rh[b]	P[c]	Rh[d]	P[d]
Ia[e]	.59	.37	.05	.34	.07
Ib	.59	.28	.26		
IIa[f]	.2			.06	.04
IIb	.2	.15	.11	.13	.10
IIc	.2		.10	.12	.06
IId	.2			.03	.02
IIe	.2			.03	.01
IIf	.2			.06	.04
IIg	.2			.10	.06
IIIa[g]	.43		.11	.44	.35
IIIb	.43	.15	.04	.18	.10
IIIc	.43	.14	.06	.21	.16

a) Determined from elemental analysis for N.
b) Determined from neutron activation analysis for Rh.
c) Determined for elemental analysis for P.
d) Calculated from visible spectra.
e) 2% crosslinked resins, 200-400-mesh.
f) 5% crosslinked resins, 60-80 mesh.
g) 8% crosslinked resins, 80-150 mesh. Sample IIIa was produced using twice the initial 'Rh(CO)$_2$Cl]$_2$ concentration used for IIIb and IIIc.

Table III. Results of the Catalytic Hydrogenation of Several
Substrates with $\textcircled{P}$-bipyPtCl$_2$.

Substrate	% Yield		Substrate	% Yield
1-Hexene	90		Trans-2-Hexene	5
Cis & Trans-2-Hexene	5		Cyclohexene	5
1-Heptyne	Ane: 58		1,3-COD	very small
	Ene: 42		1,5-COD	

TABLE III.

Table IV. Results of the Catalytic Hydrogenations of Several
Subtrates with (P)-bipyPdCl$_2$.

Substrate		% Yield
1-Hexene		70
Trans-2-Hexene		35
Cis & Trans-2-Hexene		40
Cyclohexene		60
1,5-COD	alkane	10
	alkene	90
1,3-COD	alkane	2
	alkene	98
1-Heptyne	alkane	61
	alkene	39
Methyl acrylate		not quantitated
Benzyl chloride		100
Nitrobenzene		not quantitated

TABLE IV.

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